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Evidence from pressure-dependent NMR for a percolative phase transition in $KTa_{1-x}Nb_xO_3$

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NMR signal intensities of ^{181}Ta in two crystals of $KTa_{1-x}Nb_xO_3$ (KTN) ($x=0.021$, 0.033; 10 K$<T<200$ K and $p\leq 4$ kbar) are compared with predictions of a continuum percolation model, using parameters extrapolated from pressure-dependent dielectric data in the literature ($x=0.012$, 0.023). The essential observation is that at low temperature, a p- and x-dependent fraction of $KTaO_3$ unit cells remains unpolarized. The (p,x) variation of this fraction can be explained by the percolation model. Extrapolation to $x=0$ predicts a phase transition at zero K for negative pressures, in quantitative agreement with an analysis of available data (at positive p) for pure $KTaO_3$.

INTRODUCTION

The phase diagram of potassium tantalate niobate ($KTa_{1-x}Nb_xO_3$, KTN) at low Nb concentrations ($x<0.04$) has been studied in some detail by Boatner, Höchli, and Weibel.[1,2] Evidence for a phase transition comes from hysteresis loops,[1] the dielectric constant,[2] the elastic constant,[2] birefringence,[3] nuclear-spin-lattice relaxation and the NMR spectra of ^{93}Nb and ^{181}Ta.[4,5] However, it has proven impossible to detect a change in structure using high-resolution x-ray diffraction,[6] and the nature of the transition continues to be discussed.[7] Using ^{181}Ta NMR we have shown earlier[4] that a fraction of the crystal's volume remains unpolarized, even far below the transition temperature. More precisely, a given $KTaO_3$ unit cell remains unpolarized if its (roughly) 10^2 nearest-neighbor unit cells all contain Ta (and no Nb); otherwise it is polarized. We remarked that this number is comparable to the reciprocal of the Nb concentration ($x=0.008$) for which the transition disappears at zero pressure. Uwe *et al.* have proposed more explicitly that there is a correlation between the concentration of Nb needed to obtain a phase transition in KTN at a given temperature and the size of ferroelectric microregions in pure $KTaO_3$ at the same temperature.[8]

The existence of unpolarized regions in the low-temperature phase of KTN suggests that the phase transition occurs through continuum percolation: around random points of a cubic lattice (the Nb sites), polar microregions start to grow with decreasing temperatures as a consequence of the increase of the polar correlation length of the host lattice. When the microregions overlap in an infinite cluster, they are frozen and all Nb and Ta ions in the cluster go off center. Those Ta ions that are not in the cluster continue to give an observable NMR signal. It has been shown by Samara that the minimum concentration of Nb needed to observe a phase transition increases with increasing hydrostatic pressure.[9] Our continuum-percolation model then predicts that the low-temperature ^{181}Ta NMR intensity must increase with increasing pressure, reflecting a diminishing correlation length.

In the following we first present some properties of pure potassium tantalate that can be derived from literature data and that will be useful for our purpose. Next we recall for convenience the dielectric and the ^{181}Ta NMR results on KTN atmospheric pressure ("zero pressure"). Then we analyze Samara's pressure-dependent dielectric data, in particular to find the $p(x,T=0)$ relation: the pressure needed to bring the transition temperature to 0 K for a given concentration x. This relation is compared with our pressure-dependent ^{181}Ta NMR results on two samples of KTN, obtained as described in the experimental section. This comparison is the central point of the paper, a test of the percolation model. As a byproduct we propose an empirical expression for $T(p,x)$, the pressure- and concentration-dependent transition temperature in KTN, related to the p and T dependence of the correlation length in pure $KTaO_3$.

Throughout this paper we will neglect problems of dynamics, dielectric dispersion, etc., and avoid discussion of the "nature" of the low-temperature phase (quantum ferroelectric, dipole glass, etc.). We stress however the importance of the experimental fact that the crystals remain locally unpolarized.

PROPERTIES OF $KTa_{1-x}Nb_xO_3$

Below room temperature, the static dielectric constant ε of pure potassium tantalate ($x=0$) is well described by Barrett's quantum harmonic oscillator version[10] of Slater's mean-field theory[11]

$$\varepsilon = A + \frac{B}{(T_1/2)\coth(T_1/2T)-T_2} \; . \tag{1}$$

Here A and B are independent of temperature and determined by lattice geometry and the different ionic polarizabilities. Abel[12] has determined the pressure dependence of the parameters T_1 and T_2. Extrapolating these results towards negative pressures (crystal in extension rather than in compression) and setting the denominator in the rightmost term of Eq. (1) to zero, we find the phase diagram shown in Fig. 1. In agreement with this figure, Postnikov *et al.*[13] have recently calculated that for a 5% expanded lattice (the smallest expansion considered) the ground state is ferroelectric.

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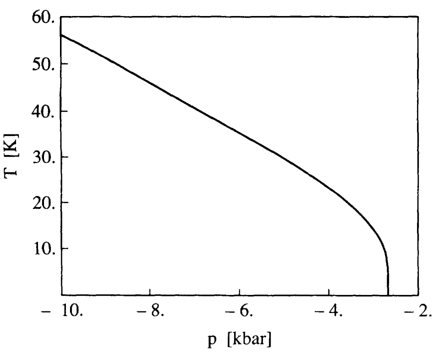

FIG. 1. Phase diagram of pure $KTaO_3$. The lower left part has a ferroelectric ground state. Extrapolated from dielectric data at positive pressures by Abel (Ref. 12).

Although negative hydrostatic pressures may be difficult to realize, the phase diagram of Fig. 1 is perfectly acceptable, and we expect all usual properties to hold: in particular that at the transition the polar correlation length ξ goes to infinity (in this paper we will more often use the correlation volume q, expressed in unit-cell volume a^3 by $qa^3=4\pi\xi^3/3$). A measure of ξ is given by the quadratic dispersion of the soft mode frequency for small wave vectors k:

$$\omega^2(k)=\omega_0^2(1+\xi^2k^2) , \tag{2}$$

where both ω_0 and ξ are temperature and pressure dependent. To obtain a rough estimate for q, we use the $(k,0,0)$ value where $\xi^2k^2=1$ in the data of Axe, Harada, and Shirane:[14] we find $q=42$ at 15 K, decreasing to 3.8 at 90 K. Another estimate comes from optical experiments. Using Raman spectroscopy, Uwe *et al.*[8] detect the existence of microscopic ferroelectric regions in nominally pure $KTaO_3$. Their size increases with decreasing temperatures, and is of the order of 200 unit cells at 0 K. From hyper-Rayleigh scattering, Vogt[15] finds polarized microregions that expand with decreasing temperature in proportionality to the inverse of the soft-mode frequency; since in $KTaO_3$ the product $\omega_0^2\xi^2$ varies only slowly with temperature,[8] this amounts to a linear variation with correlation length. It is believed that, although the existence of such microregions is almost surely due to extrinsic defects,[16] their size is an intrinsic property of the potassium tantalate lattice.

In the case of KTN, the initial work by Höchli, Weibel, and Boatner[2] was guided by theoretical considerations based on the virtual crystal approximation (VCA), treating the Nb concentration as a generalized interaction parameter. The theory then predicts a variation of transition temperature T with concentration x as

$$T=T_a(x-x_a)^{1/2} . \tag{3}$$

Fitting to experimental data, Rytz, Châtelain, and Höchli[17] obtained $T_a=276$ K, $x_a=8\times10^{-3}$. The determination of Nb concentration is not easy, and most workers actually obtain their x values from the temperature of the maximum in the dielectric constant and Eq. (3). The latter, therefore, more has the status of an axiom than of a theorem. In the following, we will argue that Eq. (3) is not compatible with Samara's findings;[9] since furthermore our NMR data cast doubt on the validity of the VCA in KTN,[4] we will propose that Eq. (3) is not strictly valid.

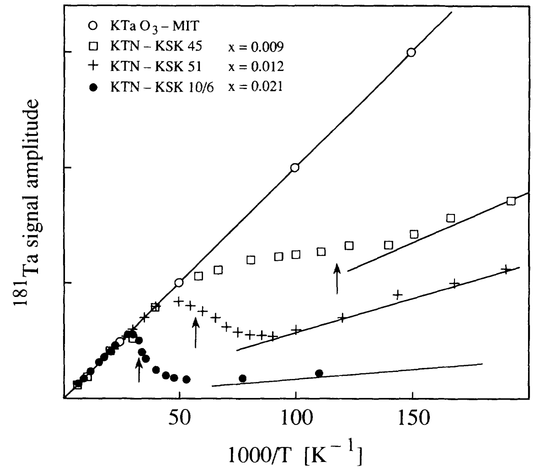

FIG. 2. Temperature dependence of the ^{181}Ta NMR signal intensity in $KTaO_3$ and in several KTN samples. Vertical scale different for different samples. The straight lines represent Curie-type paramagnetism. All data at atmospheric pressure. The sample numbering in this and the following figures is the same as that of Refs. 4, 5, and 17.

As shown in Fig. 2, at high temperatures T, the ^{181}Ta NMR signal amplitudes in the different crystals are inversely proportional to T, as expected from Curie's law. In that figure, the vertical scale is different for different samples, but corresponds to within reproducibility (±15%, including reproduction of NMR probe tuning) to what would be expected from their weight. The uncertainty implies that in the high-temperature phase of KTN, the ^{181}Ta NMR from between five and ten unit cells around a Nb impurity may be (but not necessarily is) perturbed. This possibility will be neglected in the following discussion, since it would not qualitatively alter its conclusions.

Also in Fig. 2, it is seen that at low temperatures, not all the ^{181}Ta NMR signal disappears from the NMR frequency window: a part of it remains at the same frequency, and finally follows again Curie's law but with a smaller constant. (We will call the ratio of the two Curie constants the relative zero-temperature signal intensity S). That these nuclei do not change their NMR frequency proves immediately that they remain in a locally cubic environment. That they pick up a new Curie's law shows that at low temperatures their number does not change. For a quantitative analysis, we use an "all-or-nothing" model (for a schematic see Fig. 3): the frequencies of all ^{181}Ta nuclei that are within a correlation volume q around a Nb ion are shifted out of the frequency window; only those Ta that do not have any Nb ion among their q nearest neighbors remain visible (and correspond to nonpolarized unit cells). The relative zero-temperature signal

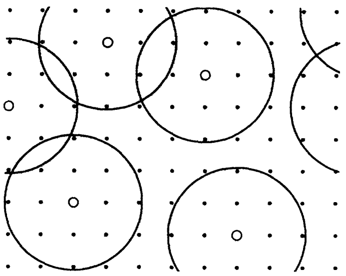

FIG. 3. Sketch of the polarization in the low-temperature phase of KTN. Around each Nb ion (open circles) a polarized volume of $KTaO_3$ is formed (grey spheres). The positions of Ta ions are indicated by dots. Only Ta ions outside the grey areas contribute to the NMR signal.

intensity S (or nonpolarized volume fraction) is given as function of Nb concentration x by (see Fig. 4)

$$S=(1-x)^q , \tag{4a}$$

$$-\ln S=qx . \tag{4b}$$

In a rigorous all-or-nothing model, q should be independent of x. The experimental data seem to indicate a slight interaction effect, especially at higher concentrations: ^{181}Ta nuclei that are just outside two or more polarization clouds, nevertheless have their frequency shifted out of the observation window:

$$-\ln S=qx+cx^2\equiv xw_0(x) , \tag{5}$$

where the experimental values are $q=63$ and $c=2900$; the rightmost member defines the "wipeout number" $w_0(x)$ for later use.

By the percolation hypothesis, the correlation volume $q(p,T)$ at a given p and T is inversely proportional to the Nb concentration $x(p,T)$ needed to obtain a phase transition at that same p and T; denoting the proportionality constant d:

$$q(p,T)=dx^{-1}(p,T) . \tag{6}$$

For comparison with the pressure-dependent NMR data, we will need $q(p,0)$ [compare Eq. (5), where $q\equiv q(0,0)$], or equivalently $x(p,0)$. Extrapolating Samara's pressure-dependent data[9] for $x=0.012$ and $x=0.023$ [using Eq. (3), rather than the nominal value $x=0.02$] to 0 K, we obtain $x(p,0)$ for the two values of x; a third value is given by the conventional Eq. (3) at $p=0$. Furthermore we have the point $x=0$ at $p=-2.7$ kbar from Fig. 1. As shown in Fig. 5, these four data points define a straight line:

$$x(p,0)/x_0=1+p/p_0 \tag{7}$$

with $p_0=3.12$ kbar and $x_0=0.0067$. Eq. (6) becomes

$$q(p,0)=\frac{d/x_0}{(p/p_0)+1} . \tag{8}$$

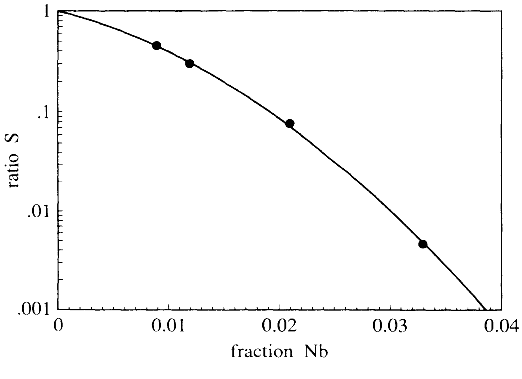

FIG. 4. The ratio S of the low- and the high-temperature Curie constants in Fig. 2 as a function of Nb concentration. The curve is given by Eq. (5). Adapted from Ref. 4, with corrections. The data for $x=0.033$ are from Fig. 6.

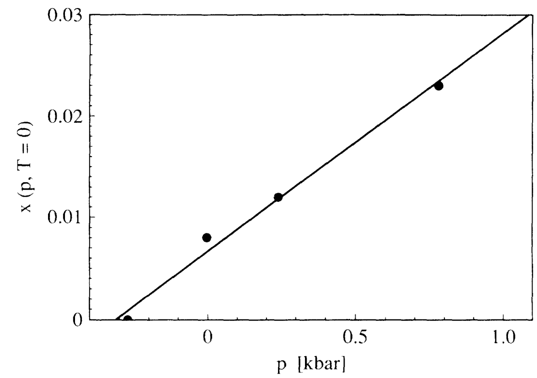

FIG. 5. The concentration $x(p,T=0)$ of Nb ions in KTN at which the transition temperature equals 0 K as a function of pressure. The line is given by Eq. (7).

The latter quantity should be accessible through pressure-dependent NMR: we write a generalization of Eq. (4b) as

$$-\ln S(x,p)=xw(x,p) \tag{9a}$$

and, by analogy with Eq. (8):

$$w(x,p)=\frac{w_0(x)}{(p/p_0)+1} . \tag{9b}$$

EXPERIMENTAL

The cylindrical pressure bomb is made from CuBe alloy (Berylco 25 4/4 H), outside diameter 46 mm, sample space diameter 20 mm. The rf feedthrough is patterned after a design by Schouten, Trappeniers, and Goedegebuure.[18] The bomb is inserted in a He flow cryostat (Oxford), and the temperature on the bomb's outside measured by a carbon glass resistor (Lake Shore CGR 1-3000). The samples may have been one or two degrees warmer than the indicated temperatures. The pressure medium was He, using a standard two-stage pressure generator (Nova). The pressure was read on this unit; due to solidification of He, the actual pressure in the sample chamber is expected to diminish with diminishing temperature. These uncertainties in the values of temperature and pressure at the sample are unavoidable, due to geometrical restrictions inside our 8-T NMR magnet (Oxford), and are the likely cause that the expected low-temperature Curie's laws for the ^{181}Ta NMR signal intensity are rather less well-defined in the present experiments than they were in our atmospheric pressure work.[4] For safety reasons, the NMR probe tuning and the cryostat's flow control were remotely operated; otherwise the equipment and the NMR techniques were the same as used earlier. The single-crystal samples have been grown by a slow-cooling method, except the reference crystal $KTaO_3$-MIT. The sample numbering is the same as that of Refs. 4, 5, and 17. (Further references to sample preparation may also be found in Ref. 17.) Except for some defects near surfaces and edges, all crystals were optically opaque between crossed polarizers. The concentrations of Nb cited have been determined from dielectric experiments on the samples themselves.

NMR RESULTS AND DISCUSSION

Due to experimental problems (cf. Experimental section), the data in Fig. 6 are not as easy to analyze as the earlier ones at atmospheric pressure in Fig. 2, but we can show that they are compatible with the percolation hypothesis. With $w_0(x)$ [cf. Eq. (5)] determined from reasonably accurate NMR experiments at zero pressure (see Fig. 2), and p_0 from Fig. 5, we can predict from Eqs. (9) the low-temperature asymptotes of the pressure-dependent ^{181}Ta NMR signal intensities, drawn in Fig. 6. Noting that the structure of Eq. (9b) is due to an empirical fit to dielectric data (and, as far as we are aware, not immediately dictated by some general consideration), we think that the semiquantitative agreement between experiment and prediction is very clearly in favor of the percolation model. The deviations for $x = 0.033$ are probably related to uncertainty in the coefficient c of Eq. (5).

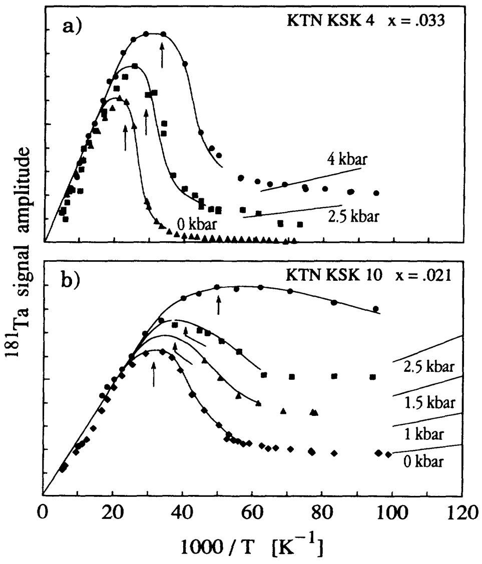

FIG. 6. Temperature dependence of the ^{181}Ta NMR signal intensity in two KTN samples, with pressure as parameter, compare Fig. 2. The straight lines indicate the expected low-temperature asymptotes at different pressures, according to Eq. (9b). The arrows indicate the expected transition temperatures according to Eq. (12).

From the NMR data and Eqs. (5) and (8) we find $d = 0.42$. For continuum percolation of randomly centered permeable spheres of uniform size, the critical concentration is 0.35.[19] This suggests that the correlation volume q' relevant for the phase transition is somewhat smaller than the correlation volume q seen by ^{181}Ta NMR. Indeed, a ^{181}Ta nucleus can be on center in its own unit cell, and have its NMR frequency perturbed by electric-field gradients due to a nearby polarized region; but it is impossible that a ^{181}Ta nucleus does not belong to the volume q (has unperturbed frequency) but nevertheless belongs to q': therefore $q' < q$.

The representation in Fig. 5 implies that by applying a suitable (positive or negative) pressure, KTN with any concentration $x \geq 0$ can be made to undergo a transition at $T \geq 0$. Samara's data obey the linear relation

$$T(x,p) = a(x) - pb(x) , \tag{10}$$

where $a(x)$ and $b(x)$ are functions of x only. If we suppose Eq. (10) to be valid for all values of x, the function $a(x)$ cannot be given by the conventional Eq. (3), which allows solutions only for $x \geq 0.008$. From Eqs. (7) and (10):

$$T(x,p=0) = \frac{p_0}{x_0}(x - x_0)b(x) , \tag{11}$$

which, on the condition that $b(x)$ is well-behaved, goes to zero for $x = 0.0067$, very close to the commonly accepted value $x = 0.008$. From trial and error (see Fig. 7) we propose $b(x)$ of the form $b/[x \ln(x_1/x)]$, and Eq. (10) becomes

$$T(x,p) = T_0 \frac{(x/x_0) - (p/p_0) - 1}{(x/x_0)\ln(x_1/x)} \tag{12}$$

with $x_1 = 0.41$, $T_0 = 138$ K, and p_0, x_0 as defined before. This expression is of course completely empirical, and its form has no theoretical justification: it simply allows consistent extrapolation of the scarce experimental data over the range of values $0 < x < 0.04$, $0 \text{ K} < T < 50$ K,

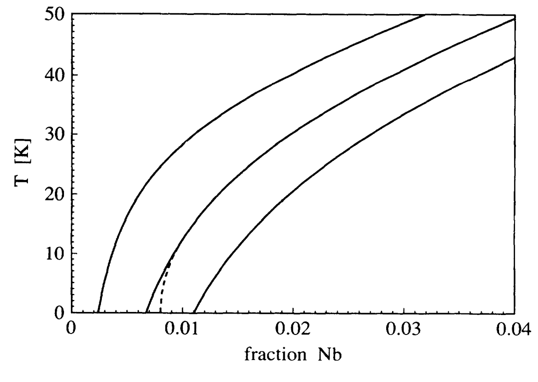

FIG. 7. The $T(x)$ phase diagram of KTN at hydrostatic pressures of -2 (top), 0 (middle), and $+2$ kbar (bottom), according to Eq. (12). The dashed line is the conventional Eq. (3).

$p > -2.7$ kbar. The transition temperatures according to Eq. (12) for the samples used in the NMR work are indicated by the arrows in Figs. 2 and 6.

According to the percolation model for the phase transition in KTN, the pressure and temperature variation of the polar correlation volume q' in pure potassium tantalate is given by Eq. (6) with $d = 0.35$, and with $x(p,T)$ obtained from experiments on KTN, or from the empirical Eq. (12). Both this percolation model and the "all-or-nothing" model used to describe the ^{181}Ta NMR signal assume sharp boundaries to the correlation volume, and a spherical shape. These are of course simplifications to obtain an easy modelization, and the absolute values following from Eqs. (6) and (12) should not be taken too literally.

CONCLUSION

The "wipeout number" w of the ^{181}Ta NMR signal intensities [Eq. (9b)] below the phase transition in KTN gives a volume fraction of the crystal that is not polarized in the low-temperature phase. At atmospheric pressure, this fraction can be determined with some precision, and its variation with Nb concentration can be described by an overlapping-spheres model, as sketched in Fig. 3, with finite-concentration corrections as in Eq. (5). This in turn suggests a continuum-percolation model for the phase transition, where the central quantity is the pressure- and temperature-dependent polar correlation volume of pure $KTaO_3$. Using this model, our atmospheric-pressure NMR data, and Abel's and Samara's pressure-dependent dielectric data for $KTaO_3$ and KTN, we predict without further adjustable constants the pressure and concentration dependence of the number w. The good agreement with experimental results, shown in Fig. 6, can be considered as strong evidence in favor of the percolation model.

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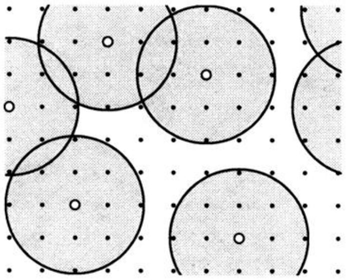

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